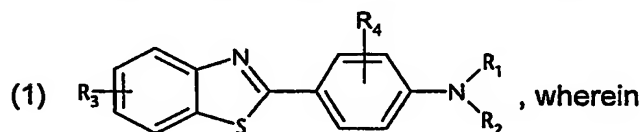


# Aminophenylbenzothiazole compounds

The present invention relates to the use of aminophenylbenzothiazole compounds as UV filters, especially for protecting human and animal hair and skin from UV radiation, to processes for the preparation of those compounds and to cosmetic preparations comprising those compounds.

The present invention relates to the use, as UV filters, of compounds of formula



R<sub>1</sub> and R<sub>2</sub> are each independently of the other hydrogen; unsubstituted or halo-, amino-, mono- or di-C<sub>1</sub>-C<sub>5</sub>alkylamino-, cyano- or C<sub>1</sub>-C<sub>5</sub>alkoxy-substituted C<sub>1</sub>-C<sub>22</sub>alkyl, C<sub>5</sub>-C<sub>10</sub>cycloalkyl, carboxy-C<sub>1</sub>-C<sub>22</sub>alkyl, carboxy-C<sub>6</sub>-C<sub>10</sub>aryl, C<sub>6</sub>-C<sub>10</sub>aryl or C<sub>6</sub>-C<sub>10</sub>aryl-C<sub>1</sub>-C<sub>5</sub>alkyl; carbamoyl; or sulfamoyl; or

R<sub>1</sub> and R<sub>2</sub>, together with the nitrogen atom linking them, form a 5- to 7-membered heterocyclic radical; and

R<sub>3</sub> is hydrogen; or C<sub>1</sub>-C<sub>22</sub>alkyl; and

R<sub>4</sub> is hydrogen; hydroxy; C<sub>1</sub>-C<sub>22</sub>alkyl; or C<sub>1</sub>-C<sub>22</sub>alkoxy.

C<sub>1</sub>-C<sub>22</sub>Alkyl radicals are straight-chain or branched alkyl radicals such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, amyl, isoamyl or tert-amyl, hexyl, 2-ethylhexyl, heptyl, octyl, isooctyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl or eicosyl.

C<sub>5</sub>-C<sub>10</sub>Cycloalkyl is, for example, cyclopentyl, cycloheptyl, cyclooctyl, cyclononyl or cyclodecyl and, especially, cyclohexyl. Those radicals may be substituted, for example by one or more identical or different C<sub>1</sub>-C<sub>4</sub>alkyl radicals, especially by methyl, and/or by hydroxy. When cycloalkyl radicals are substituted by one or more substituents, they are preferably substituted by one, two or four, especially one or two, identical or different substituents.

C<sub>6</sub>-C<sub>10</sub>Aryl is naphthyl or, especially, phenyl.

C<sub>1</sub>-C<sub>22</sub>Alkoxy radicals are straight-chain or branched radicals such as, for example, methoxy, ethoxy, propoxy, butoxy or pentyloxy, hexyloxy, heptyloxy, octyloxy, isooctyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tetradecyloxy, pentadecyloxy, hexadecyloxy, heptadecyloxy, octadecyloxy or eicosyloxy.

Heterocyclic radicals contain one, two, three or four identical or different ring hetero atoms. Special preference is given to heterocycles containing one, two or three, especially one or two, identical or different hetero atoms. The heterocycles may be mono- or poly-cyclic, for example mono-, bi- or tri-cyclic. They are preferably mono- or bi-cyclic, especially monocyclic. The rings are preferably 5-, 6- or 7-membered. Examples of monocyclic and bicyclic heterocyclic systems from which radicals occurring in the compounds of formula (1) may be derived are, for example, pyrrole, furan, thiophene, imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, pyridine, pyridazine, pyrimidine, pyrazine, pyran, thiopyran, 1,4-dioxane, 1,2-oxazine, 1,3-oxazine, 1,4-oxazine, indole, benzothiophene, benzofuran, pyrrolidine, piperidine, piperazine, morpholine and thiomorpholine.

Unsaturated heterocycles may contain, for example, one, two or three unsaturated double bonds in the ring system. 5-membered and 6-membered rings in monocyclic and polycyclic heterocycles may, especially, also be aromatic.

C<sub>6</sub>-C<sub>10</sub>Aryl and heteroaryl radicals may be unsubstituted or may carry one or more, for example one, two, three or four, identical or different substituents, which may be located in any positions. Examples of such substituents are, e.g., C<sub>1</sub>-C<sub>4</sub>alkyl, halogen, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkoxy, trifluoromethyl, cyano, hydroxycarbonyl, C<sub>1</sub>-C<sub>4</sub>alkoxycarbonyl, aminocarbonyl, amino, C<sub>1</sub>-C<sub>4</sub>alkylamino, di-C<sub>1</sub>-C<sub>4</sub>alkylamino and C<sub>1</sub>-C<sub>4</sub>alkylcarbonylamino.

Halogen is fluorine, chlorine, bromine or iodine, preferably fluorine or chlorine.

In accordance with the invention, preference is given to the use of UV filters of formula (1) wherein

R<sub>4</sub> is hydrogen.

Preference is given especially to compounds of formula (1) wherein

R<sub>1</sub> and R<sub>2</sub> are each independently of the other hydrogen; or C<sub>1</sub>-C<sub>12</sub>alkyl unsubstituted or substituted by halogen, amino, mono- or di-C<sub>1</sub>-C<sub>6</sub>alkylamino, cyano or by C<sub>1</sub>-C<sub>5</sub>alkoxy; and R<sub>3</sub> is hydrogen; or C<sub>1</sub>-C<sub>5</sub>alkyl.

Special preference is given to compounds of formula (1) wherein

R<sub>1</sub> and R<sub>2</sub> are each independently of the other hydrogen; or C<sub>1</sub>-C<sub>12</sub>alkyl; or

R<sub>1</sub> and R<sub>2</sub> together form a 5- to 7-membered heterocyclic radical;

R<sub>3</sub> is hydrogen; or C<sub>1</sub>-C<sub>5</sub>alkyl; and

R<sub>4</sub> is hydrogen.

Very special preference is given to compounds of formula (1) wherein

R<sub>1</sub> is hydrogen;

R<sub>2</sub> is C<sub>1</sub>-C<sub>12</sub>alkyl;

R<sub>3</sub> is hydrogen; or C<sub>1</sub>-C<sub>5</sub>alkyl; and

R<sub>4</sub> is hydrogen;

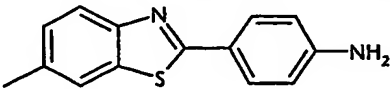
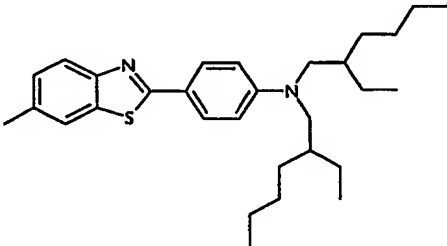
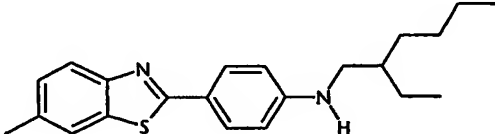
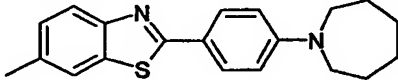
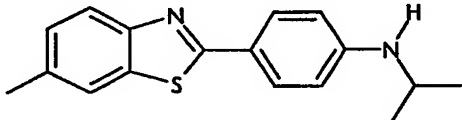
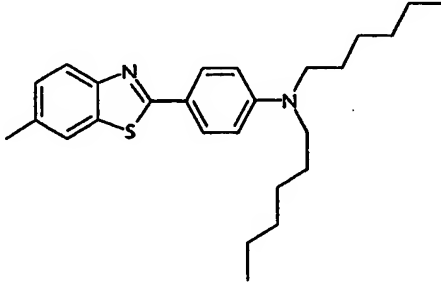
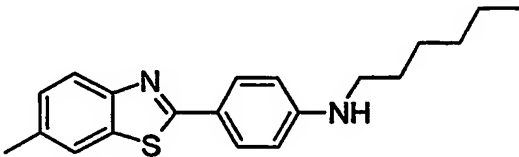
and especially to compounds of formula (1) wherein

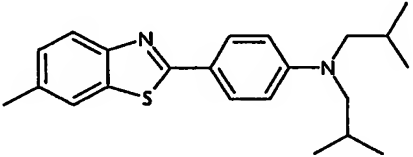
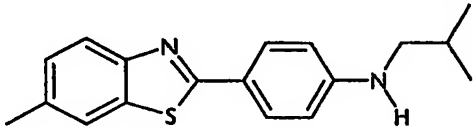
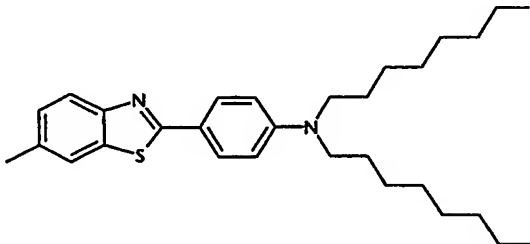
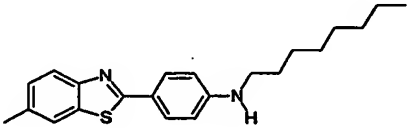
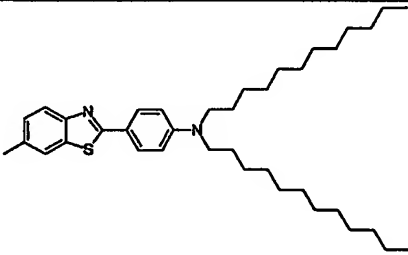
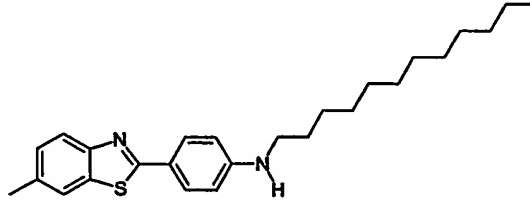
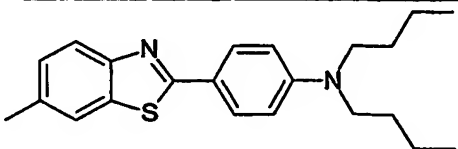
R<sub>2</sub> is branched or unbranched C<sub>6</sub>-C<sub>12</sub>alkyl; very especially n-hexyl; n-octyl; or 2-ethylhexyl.

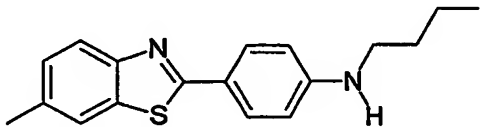
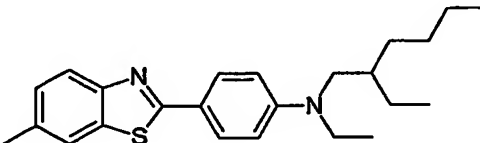
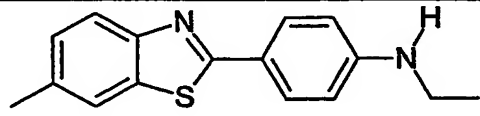
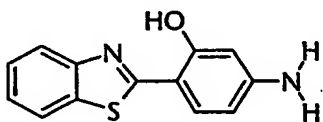
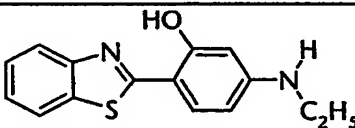
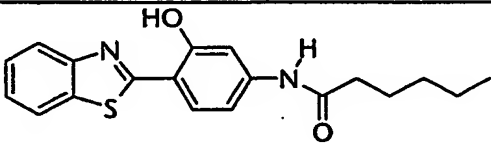
Very special preference is also given to compounds of formula (1) wherein

R<sub>4</sub> is hydroxy.

Examples of compounds used in accordance with the invention are listed in Table 1, which follows:

Comp. of formula	Structure	$\lambda_{\max}$ [nm] (EtOH)	$\epsilon$	$E$ (196, 1cm)
(2)		343	32692	1360
(3)		366	38894	837
(4)		358	39746	1127
(5)		366	42328	1313
(6)		356	42328	1397
(7)		366	44209	1082
(8)		356	38141	1175

Comp. of formula	Structure	$\lambda_{\max}$ [nm] (EtOH)	$\epsilon$	$E$ (196, 1cm)
(9)		365	38053	1079
(10)		357	22669	765
(11)		366	38237	823
(12)		356	37927	1076
(13)		366	36567	634
(14)		356	38173	934
(15)		355	41401	1174

Comp. of formula	Structure	$\lambda_{\max}$ [nm] (EtOH)	$\epsilon$	E (196, 1cm)
(16)		357	37122	1252
(17)		364	42514	1117
(18)		355	39164	1459
(19)		358	39 095	1613
(20)		381	51 869	1738
(21)		3450	35 890	1057

Aminophenylbenzothiazole compounds are known in the literature and some are commercially available.

The compounds of formula (1) according to the invention can be prepared, for example, by

condensation of  $R_3$ -substituted o-amino-thiophenols of formula  with  $R_1$ -,  $R_2$ -

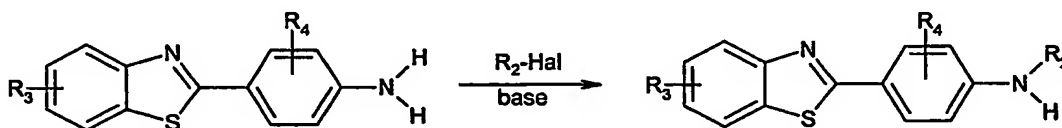
and  $R_4$ -substituted p-amino-benzaldehydes, where appropriate in the presence of an oxidising agent [R.C. Elderfield, "Heterocyclic Compounds", Vol. 5, 508 ff, O. Süss *et al*, US Patent 3 257 204 (1966), H.P. Lankelma *et al*, J. Amer. Chem. Soc. 54, 379, (1932) or Stephens *et al*, J. Chem. Soc. (1950) 1722].

Condensation of o-amino-thiophenols with  $R_1$ - and  $R_2$ -substituted p-amino-benzoic acids in accordance with L.C. Galatis, J. Amer. Chem. Soc. 70, 1967 (1948) also yields compounds of the general formula (1).

The benzothiazole compounds of the general formula (1) wherein  $R_1$  is hydrogen and  $R_2$  is an unsubstituted or substituted aralkyl radical are obtained by reaction of  $R_3$ -substituted 2-(4'-aminophenyl)-benzothiazoles with unsubstituted or substituted benzaldehydes to form the corresponding azomethines, which may be hydrogenated very simply using sodium boronate in polar solvents to form the corresponding 2-(4'-benzylaminophenyl)benzothiazole derivatives [J. H. Billmann *et al.*, J. Org. Chem. 22, 1068, (1957)].

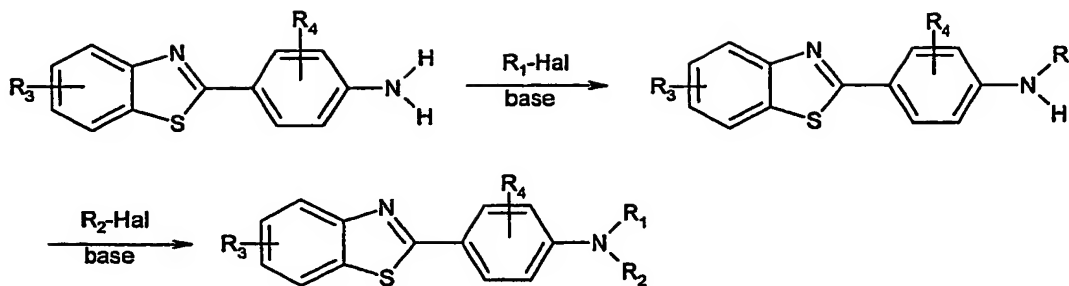
The benzothiazole compounds of the general formula (1) wherein  $R_1$  and/or  $R_2$  is/are an unsubstituted or substituted alkyl or aralkyl radical can also be prepared by direct alkylation of commercially available 2-(4-aminophenyl)-6-methylbenzothiazole. As alkylating agents there can be used, analogously to DE-OS-51738, the appropriate alcohols under the action of strong acids.

The compounds of formula (1) according to the invention wherein  $R_1$  is hydrogen are prepared from  $R_3$ -substituted 2-(4-aminophenyl)-benzothiazole by alkylation with the appropriate haloalkanes/haloaralkanes using a base, in accordance with the following Scheme:



wherein  $R_2$ ,  $R_3$  and  $R_4$  are as defined in claim 1.

The compounds of formula (1) wherein  $R_1$  and  $R_2$  are alkyl or aryl-alkyl are prepared from  $R_3$ -substituted 2-(4-aminophenyl)-benzothiazole by alkylation with the appropriate haloalkanes/haloaralkanes using a base, in accordance with the following Scheme:



$R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are defined as in claim 1.

As base there may be used a metal hydride, such as sodium hydride, an alkali metal alcoholate such as, for example, sodium methanolate, sodium ethanolate or potassium tert-butanolate, or an alkali metal hydroxide, such as sodium hydroxide or potassium hydroxide, an amine base, such as  $Et_3N$ ,  $(isoprop)_2EtN$  or quinaldine etc.. Likewise, basic ion exchangers may also be used. The reaction may also be carried out without the addition of base.

The reaction is preferably carried out in dimethyl sulfoxide, N-methylpyrrolidone, dimethylformamide or dimethylacetamide, but protic solvents, such as methanol, ethanol, isobutanol, tert-butanol or isopropanol, are also possible. In addition, the reaction may also be carried out in aliphatic or aromatic solvents, such as hexane, toluene or xylene. Ethers, such as diethyl ether and tetrahydrofuran, or halogenated solvents, such as chloroform or dichloromethane, are also possible. Likewise, solvent mixtures may also be used.

The reaction may be carried out at temperatures between  $-78^\circ\text{C}$  and the boiling point of the reaction mixture, preferably proceeding at from 10 to  $120^\circ\text{C}$ .

Usually a large excess of alkylating agent is used and alkylating agent remaining after the reaction is removed by vacuum distillation. Preference is given to the use of from 1.0 to 8.0 mol of the haloalkane/haloaralkane, based on 1 mol of aminophenylbenzothiazole.

The products are purified by recrystallisation from a suitable solvent or by column-chromatographic separation using a suitable eluant.

The invention relates also to the process for the preparation of compounds of formula(1).



The compounds of the formula (1) according to the present invention are particularly suitable as UV filters, i.e. for protecting ultraviolet-sensitive organic materials, in particular the skin and hair of humans and animals, from the harmful effects of UV radiation. These compounds are therefore suitable as sunscreens in cosmetic, pharmaceutical and veterinary medical preparations. These compounds can be used both in dissolved form and in the micronized state.

The UV absorbers according to the present invention can be used either in the dissolved state (soluble organic filters, solubilized organic filters) or in the micronised state (nanoscalar organic filters, particulate organic filters, UV-absorber pigments).

The triazine derivatives of formula (1) which have no alkyl substituents or only lower-alkyl substituents are characterized by a poor oil-solubility and a high melting point. They are therefore particularly suitable UV absorbers in the micronized state.

Any known process suitable for the preparation of microparticles can be used for the preparation of the micronised UV absorbers, for example:

- wet-milling (low viscous micronisation process for pumpable dispersions), with a hard grinding medium, for example zirconium silicate balls in a ball mill and a protective surfactant or a protective polymer in water or in a suitable organic solvent;
- wet-kneading (high viscous micronisation process for non pump-able pastes) using a continuous or discontinuous (batch) kneader. For a wet-kneading process a solvent (water or cosmetically acceptable oils), a grinding-aid (surfactant, emulsifier) and a polymeric grinding aid may be used. Both processes may be used respectively
- spray-drying from a suitable solvent, for example aqueous suspensions or suspensions containing organic solvents, or true solutions in water, ethanol, dichloroethane, toluene or N-methylpyrrolidone etc..
- by the expansion according to the RESS process (Rapid Expansion of Supercritical Solutions) of supercritical fluids (e.g. CO<sub>2</sub>) in which the UV filter or filters is/are dissolved, or the expansion of fluid carbon dioxide together with a solution of one or more UV filters in a suitable organic solvent;
- by reprecipitation from suitable solvents, including supercritical fluids (GASR process = Gas Anti-Solvent Recrystallisation / PCA process = Precipitation with Compressed Anti-solvents).

As milling apparatus for the preparation of the micronised organic UV absorbers there may be used, for example, a jet mill, ball mill, vibratory mill or hammer mill, preferably a high-speed mixing mill. Even more preferable mills are modern ball mills, manufacturers of these mill-types are for example Netzsch (LMZ-mill), Drais (DCP-viscoflow or cosmo), Bühler AG (centrifugal mills) or Bachhofer. The grinding is preferably carried out with a grinding aid. As kneading apparatus for the preparation of the micronised organic UV absorbers examples are typical sigma-hook batch kneaders but also serial batch kneaders (IKA-Werke) or continuous kneaders (Continua from Werner und Pfleiderer).

Useful low molecular weight grinding aids for all the above micronizing processes are surfactants and emulsifiers as disclosed below in the chapters "emulsifiers" and "surfactants".

Useful polymeric grinding aids for water dispersion are cosmetically acceptable water soluble polymers with MW > 5000 g/mol for example: acrylates (Salcare types), modified or non-modified polysaccharides, polyglucosides or xanthan gum. Furthermore an alkylated vinylpyrrolidone polymer, a vinylpyrrolidone/vinyl acetate copolymer, an acyl glutamate, an alkyl polyglucoside, cetareth-25 or a phospholipid may be used. Oil dispersions may contain cosmetically acceptable waxy polymers or natural waxes as polymeric grinding aid to adjust viscosity during and after processing.

Useful solvents are water, brine, (poly-)ethyleneglycol or glycerine for water-soluble dispersions and also cosmetically acceptable oils as described under "emollients" for oil-soluble dispersions.

The micronised UV absorbers so obtained usually have an average particle size from 0.02 to 2 micrometers, preferably from 0.05 to 1.5 micrometer and more especially from 0.1 to 1.0 micrometers.

The UV absorbers can also be used dry in powder form. For that purpose the UV absorbers are subjected to known grinding methods, such as vacuum atomization, countercurrent spray-drying etc.. Such powders have a particle size of from 0.1 to 2 micrometers. To avoid the occurrence of agglomeration, the UV absorbers can be coated with a surface-active

compound prior to the pulverization process, for example with an anionic, non-ionic or amphoteric surfactant, e.g. a phospholipid or a known polymer, such as PVP, an acrylate etc.

The cosmetic formulations or pharmaceutical compositions according to the present invention can also contain one or more than one further UV filter as described in Tables 1–3.

The cosmetic or pharmaceutical preparations can be prepared by physically mixing the UV absorber(s) with the adjuvant using customary methods, for example by simply stirring together the individual components, especially by making use of the dissolution properties of already known cosmetic UV absorbers, for example octyl methoxy cinnamate, salicylic acid isooctyl ester, etc. The UV absorber can be used, for example, without further treatment, or in the micronised state, or in the form of a powder.

Cosmetic or pharmaceutical preparations contain from 0.05–40% by weight, based on the total weight of the composition, of one UV absorber or UV absorber mixtures.

Preference is given to the use of mixing ratios of the UV absorber of formula (1) according to the present invention and optionally further light-protective agents (as described in table 1-3) from 1:99 to 99:1, especially from 1:95 to 95:1 and preferably from 10:90 to 90:10, based on weight. Of special interest are mixing ratios of from 20:80 to 80:20, especially from 40:60 to 60:40 and preferably approximately 50:50. Such mixtures can be used, *inter alia*, to improve solubility or increase UV absorption.

The UV absorbers of formula (1) according to the present invention or combinations of UV filters are useful for the protection of skin, hair and/or natural or artificial hair color.

**Table 1. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention**

p-aminobenzoic acid derivatives, for example 4-dimethylaminobenzoic acid 2-ethylhexyl ester;

salicylic acid derivatives, for example salicylic acid 2-ethylhexyl ester;  
benzophenone derivatives, for example 2-hydroxy-4-methoxybenzophenone and its 5-sulfonic acid derivative;

dibenzoylmethane derivatives, for example 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione;

diphenylacrylates, for example 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, and 3-(benzofura-

<b>Table 1. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention</b>
nyl) 2-cyanoacrylate;
3-imidazol-4-ylacrylic acid and esters;
benzofuran derivatives, especially 2-(p-aminophenyl)benzofuran derivatives, described in EP-A-582 189, US-A-5 338 539, US-A-5 518 713 and EP-A-613 893;
polymeric UV absorbers, for example the benzylidene malonate derivatives described in EP-A-709 080;
cinnamic acid derivatives, for example the 4-methoxycinnamic acid 2-ethylhexyl ester and isoamyl ester or cinnamic acid derivatives described in US-A-5 601 811 and WO 97/00851;
camphor derivatives, for example 3-(4'-methyl)benzylidene-bornan-2-one, 3-benzylidene-bornan-2-one, N-[2(and 4)-2-oxyborn-3-ylidene-methyl]-benzyl]acrylamide polymer, 3-(4'-trimethylammonium)-benzylidene-bornan-2-one methyl sulfate, 3,3'-(1,4-phenylenedimethine)-bis(7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptane-1-methanesulfonic acid) and salts, 3-(4'-sulfo)benzylidene-bornan-2-one and salts; camphorbenzalkonium methosulfate;
hydroxyphenyltriazine compounds, for example 2-(4'-methoxyphenyl)-4,6-bis(2'-hydroxy-4'-n-octyloxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(2-ethyl-hexyloxy)-2-hydroxy]-phenyl]-6-[4-(2-methoxyethyl-carboxyl)-phenylamino]-1,3,5-triazine; 2,4-bis[[4-(tris(trimethylsilyloxy-silyl)propyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(2"-methylpropenyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(1',1',1',3',5',5',5'-heptamethyltrisilyl-2"-methyl-propyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl]-6-[4-ethylcarboxy)-phenylamino]-1,3,5-triazine;
benzotriazole compounds, for example 2,2'-methylene-bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol;
trianilino-s-triazine derivatives, for example 2,4,6-trianiline-(p-carbo-2'-ethyl-1'-oxy)-1,3,5-triazine and the UV absorbers disclosed in US-A-5 332 568, EP-A-517 104, EP-A-507 691, WO 93/17002 and EP-A-570 838;
2-phenylbenzimidazole-5-sulfonic acid and salts thereof;
menthyl o-aminobenzoates;
physical sunscreens coated or not as titanium dioxide, zinc oxide, iron oxides, mica, MnO, Fe <sub>2</sub> O <sub>3</sub> , Ce <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub> . (surface coatings: polymethylmethacrylate, methicone (methyl-hydrogenpolysiloxane as described in CAS 9004-73-3), dimethicone, isopropyl titanium triisostearate (as described in CAS 61417-49-0), metal soaps as magnesium stearate (as described in CAS 4086-70-8), perfluoroalcohol phosphate as C9-15 fluoroalcohol phosphate (as described in CAS 74499-44-8; JP 5-86984, JP 4-330007)). The primary particle size is an average of 15nm-35nm and the particle size in dispersion is in the range of 100nm - 300nm.
aminohydroxy-benzophenone derivatives disclosed in DE 10011317, EP 1133980 and EP 1046391
phenyl-benzimidazole derivatives as disclosed in EP 1167358

**Table 1. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention**

the UV absorbers described in "Sunscreens", Eds. N.J. Lowe, N.A. Shaath, Marcel Dekker, Inc., New York and Basle or in Cosmetics & Toiletries (107), 50ff (1992) also can be used as additional UV protective substances.

**Table 2. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention are described in the following patents**

(Abbreviations T: table, R: row, Comp: compound, Ex: compound(s) of patent example, p: page)

DE 100331804	Tab 1 p 4, tab 2 + 3 p 5
EP 613893	Ex 1-5 + 15, T 1, pp 6-8
EP 1000950	Comp. in table 1, pp 18-21
EP 1005855	T 3, p 13
EP 1008586	Ex 1-3, pp 13-15
EP 1008593	Ex 1-8, pp 4-5
EP 1027883	Compound VII, p 3
EP 1027883	Comp I-VI, p 3
EP 1028120	Ex 1-5, pp 5-13
EP 1059082	Ex 1; T 1, pp 9-11
EP 1060734	T 1-3, pp 11-14
EP 1064922	Compounds 1-34, pp 6-14
EP 1081140	Ex 1-9, pp 11-16
EP 1103549	Compounds 1-76, pp 39-51
EP 1108712	4,5-Dimorpholino-3-hydroxypyridazine
EP 1123934	T 3, p 10
EP 1129695	Ex 1-7, pp 13-14
EP 1167359	Ex 1 p11 and ex 2 p 12
EP 420707 B1	Ex 3, p 13 (CAS Regno 80142-49-0)
EP 503338	T 1, pp 9-10
EP 517103	Ex 3,4,9,10 pp 6-7
EP 517104	Ex 1, T 1, pp 4-5; Ex 8, T 2, pp 6-8
EP 626950	all compounds
EP 669323	Ex 1-3, p 5
EP 780382	Ex 1-11, pp 5-7

**Table 2. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention are described in the following patents**  
(Abbreviations T: table, R: row, Comp: compound, Ex: compound(s) of patent example, p: page)

EP 823418	Ex 1-4, pp 7-8
EP 826361	T 1, pp 5-6
EP 832641	Ex 5+6 p 7; t 2, p 8
EP 832642	Ex 22, T 3 pp, 10-15; T 4, p 16
EP 852137	T 2, pp 41-46
EP 858318	T 1, p 6
EP 863145	Ex 1-11, pp 12-18
EP 895776	Comp. in rows 48-58, p 3; R 25+33, p 5
EP 911020	T 2, p 11-12
EP 916335	T 2-4, pp 19-41
EP 924246	T 2, p 9
EP 933376	Ex 1-15, pp 10-21
EP 944624	Ex 1+2, pp13-15
EP 945125	T 3 a+b, pp 14-15
EP 967200	Ex 2; T 3-5, pp 17-20
EP 969004	Ex 5, T 1, pp 6-8
JP 2000319629	CAS Reg. No. 80142-49-0, 137215-83-9, 307947-82-6
US 5635343	all compounds on pp 5-10
US 5338539	Ex 1-9, pp 3+4
US 5346691	Ex 40, p 7; T 5, p 8
US 5801244	Ex 1-5, pp 6-7
WO 0149686	Ex 1-5, pp 16-21
WO 0168047	Tables on pp 85-96
WO 0181297	Ex 1-3 pp 9-11
WO 0238537	All compounds p 3, compounds on rows 1-10 p 4
WO 9217461	Ex 1-22, pp 10-20
WO 9220690	Polymeric comp in examples 3-6
WO 9301164	T 1+2, pp 13-22
WO 9714680	Ex 1-3, p 10

**Table 3. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention**

No.	Chemical Name	CAS No.
1	(+/-)-1,7,7-trimethyl-3-[(4-methylphenyl)methylene]bicyclo[2.2.1]heptan-2-one	36861-47-9
2	1,7,7-trimethyl-3-(phenylmethylene)bicyclo[2.2.1]heptan-2-one	15087-24-8
3	(2-Hydroxy-4-methoxyphenyl)(4-methylphenyl)methanone	1641-17-4
4	2,4-dihydroxybenzophenone	131-56-6
5	2,2',4,4'-tetrahydroxybenzophenone	131-55-5
6	2-Hydroxy-4-methoxy benzophenone;	131-57-7
7	2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid	4065-45-6
8	2,2'-dihydroxy-4,4'-dimethoxybenzophenone	131-54-4
9	2,2'-Dihydroxy-4-methoxybenzophenone	131-53-3
10	Alpha-(2-oxoborn-3-ylidene)toluene-4-sulphonic acid and its salts	56039-58-8
11	1-[4-(1,1-dimethylethyl)phenyl]-3-(4-methoxyphenyl)propane-1,3-dione	70356-09-1
12	Methyl N,N,N-trimethyl-4-[(4,7,7-trimethyl-3-oxobicyclo[2,2,1]hept-2-ylidene)methyl]anilinium sulphate;	52793-97-2
22	3,3,5-Trimethyl cyclohexyl-2-hydroxy benzoate	118-56-9
23	Isopentyl p-methoxycinnamate	71617-10-2
27	Menthyl-o-aminobenzoate	134-09-8
28	Menthyl salicylate	89-46-3
29	2-Ethylhexyl 2-cyano,3,3-diphenylacrylate	6197-30-4
30	2- ethylhexyl 4- (dimethylamino)benzoate	21245-02-3
31	2- ethylhexyl 4- methoxycinnamate	5466-77-3
32	2- ethylhexyl salicylate	118-60-5
33	Benzoic acid, 4, 4', 4''- (1, 3, 5- triazine- 2, 4, 6- triyltriimino)tris- , tris(2- ethylhexyl) ester; 2,4,6-Trianilino-(p-carbo-2'-ethylhexyl-1'-oxi)-1,3,5-triazine	88122-99-0
34	4- aminobenzoic acid	150-13-0
35	Benzoic acid, 4-amino-, ethyl ester, polymer with oxirane	113010-52-9
38	2- phenyl- 1H- benzimidazole- 5- sulphonic acid	27503-81-7
39	2-Propenamide, N-[[4-[(4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-ylidene)methyl]phenyl]methyl]-, homopolymer	147897-12-9
40	Triethanolamine salicylate	2174-16-5
41	3, 3'- (1, 4- phenylenedimethylene)bis[7, 7- dimethyl- 2- oxo- bicyclo[2.2.1]heptane- 1- methanesulfonic acid]	90457-82-2

Table 3. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention

42	Titanium dioxide	13463-67-7
44	Zinc oxide	1314-13-2
45	2,2'-Methylene-bis-[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethyl-butyl)-phenol]	103597-45-1
46	2,4-bis[[4-(2-ethylhexyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-(1,3,5)-triazine	187393-00-6
47	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt	180898-37-7
48	Benzoic acid, 4,4'-[[6-[[4-[[[(1,1-dimethylethyl)amino]carbonyl]phenyl]amino]1,3,5-triazine-2,4-diyl]diimino]bis-, bis(2-ethylhexyl)ester	154702-15-5
49	Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]-	155633-54-8
50	alpha-(trimethylsilyl)-omega-(trimethyl-silyloxy)poly[oxy(dimethyl)-silylene]-co-[oxy(methyl)(2-{p-[2,2-bis(ethoxycarbonyl)vinyl]-phenoxy}-1-methyleneethyl)silylene]-co-[oxy(methyl)(2-{p-[2,2-bis(ethoxycarbonyl)vinyl]phenoxy}prop-1-enyl)silylene]	207574-74-1
51	Benzenesulfonic acid, 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-, monosodium salt	92484-48-5
52	Benzoic acid, 2-[4-(diethylamino)-2-hydroxybenzoyl]-, hexyl ester	302776-68-7
53	1-Dodecanaminium, N-[3-[[4-(dimethylamino)benzoyl]amino]propyl]-N,N-dimethyl-, salt with 4-methylbenzenesulfonic acid (1:1)	156679-41-3
54	1-Propanaminium, N,N,N-trimethyl-3-[(1-oxo-3-phenyl-2-propenyl)-amino]-, chloride	177190-98-6
55	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-	170864-82-1
56	1,3,5-Triazine, 2,4,6-tris(4-methoxyphenyl)-	7753-12-0
57	1,3,5-Triazine, 2,4,6-tris[4-[(2-ethylhexyl)oxy]phenyl]-	208114-14-1
58	1-Propanaminium, 3-[[3-[3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]amino]-N,N-diethyl-N-methyl-, methyl sulfate (salt)	340964-15-0
59	2-Propenoic acid, 3-(1H-imidazol-4-yl)-	104-98-3
60	Benzoic acid, 2-hydroxy-, [4-(1-methylethyl)phenyl]methyl ester	94134-93-7
61	1,2,3-Propanetriol, 1-(4-aminobenzoate)	136-44-7
62	Benzeneacetic acid, 3,4-dimethoxy-a-oxo-	4732-70-1
63	2-Propenoic acid, 2-cyano-3,3-diphenyl-, ethyl ester	5232-99-5

Suitable UV filter substances which can additionally be used with the UV absorbers according to the present invention are any UV-A and UV-B filter substances.



The cosmetic or pharmaceutical preparations may be, for example, creams, gels, lotions, alcoholic and aqueous/alcoholic solutions, emulsions, wax/fat compositions, stick preparations, powders or ointments. In addition to the above mentioned UV filters, the cosmetic or pharmaceutical preparations may contain further adjuvants as described below.

As water- and oil-containing emulsions (e.g. W/O, O/W, O/W/O and W/O/W emulsions or microemulsions) the preparations contain, for example, from 0.1 to 30 % by weight, preferably from 0.1 to 15 % by weight and especially from 0.5 to 10 % by weight, based on the total weight of the composition, of one or more UV absorbers, from 1 to 60 % by weight, especially from 5 to 50 % by weight and preferably from 10 to 35 % by weight, based on the total weight of the composition, of at least one oil component, from 0 to 30 % by weight, especially from 1 to 30 % by weight and preferably from 4 to 20 % by weight, based on the total weight of the composition, of at least one emulsifier, from 10 to 90 % by weight, especially from 30 to 90 % by weight, based on the total weight of the composition, of water, and from 0 to 88.9 % by weight, especially from 1 to 50 % by weight, of further cosmetically acceptable adjuvants.

The cosmetic or pharmaceutical compositions/preparations according to the invention may also contain one or one more additional compounds as described below.

#### Fatty alcohols

Guerbet alcohols based on fatty alcohols having from 6 to 18, preferably from 8 to 10 carbon atoms including cetyl alcohol, stearyl alcohol, cetearyl alcohol, oleyl alcohol, octyldodecanol, benzoate of C12-C15 alcohols, acetylated lanolin alcohol, etc..

#### Esters of fatty acids

Esters of linear C<sub>6</sub>-C<sub>24</sub> fatty acids with linear C<sub>3</sub>-C<sub>24</sub> alcohols, esters of branched C<sub>6</sub>-C<sub>13</sub> carboxylic acids with linear C<sub>6</sub>-C<sub>24</sub> fatty alcohols, esters of linear C<sub>6</sub>-C<sub>24</sub> fatty acids with branched alcohols, especially 2-ethylhexanol, esters of hydroxycarboxylic acids with linear or branched C<sub>6</sub>-C<sub>22</sub> fatty alcohols, especially dioctyl malates, esters of linear and/or branched fatty acids with polyhydric alcohols (for example propylene glycol, dimer diol or trimer triol) and/or Guerbet alcohols, for example caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselinic acid, linoleic acid, linolenic acid, elaeo-

stearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid and technical-grade mixtures thereof (obtained, for example, in the pressure removal of natural fats and oils, in the reduction of aldehydes from Roelen's oxosynthesis or in the dimerisation of unsaturated fatty acids) with alcohols, for example, isopropyl alcohol, caproic alcohol, capryl alcohol, 2-ethylhexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linoyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachidyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and technical-grade mixtures thereof (obtained, for example, in the high-pressure hydrogenation of technical-grade methyl esters based on fats and oils or aldehydes from Roelen's oxosynthesis and as monomer fractions in the dimerisation of unsaturated fatty alcohols).

Examples of such ester oils are isopropyl myristate, isopropyl palmitate, isopropyl stearate, isopropyl isostearate, isopropyl oleate, n-butyl stearate, n-hexyl laurate, n-decyl oleate, iso-octyl stearate, iso-nonyl stearate, isononyl isononanoate, 2-ethylhexyl palmitate, 2-hexyllaurate, 2-hexyldecyl stearate, 2-octyldodecyl palmitate, oleyl oleate, oleyl erucate, erucyl oleate, erucyl erucate, cetearyl octanoate, cetyl palmitate, cetyl stearate, cetyl oleate, cetyl behenate, cetyl acetate, myristyl myristate, myristyl behenate, myristyl oleate, myristyl stearate, myristyl palmitate, myristyl lactate, propylene glycol dicaprylate/caprinate, stearyl heptanoate, diisostearyl malate, octyl hydroxystearate, etc..

#### Other adjuvants

diethylhexyl 2,6- naphthalate, di-n-butyl adipate, di(2-ethylhexyl)-adipate, di(2-ethylhexyl)-succinate and diisotridecyl acetate, and also diol esters, such as ethylene glycol dioleate, ethylene glycol diisotridecanoate, propylene glycol di(2-ethylhexanoate), propylene glycol diisostearate, propylene glycol dipelargonate, butanediol diisostearate and neopentyl glycol dicaprylate. Esters of  $C_6$ - $C_{24}$  fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, saturated and/or unsaturated, especially benzoic acid, esters of  $C_2$ - $C_{12}$ dicarboxylic acids with linear or branched alcohols having from 1 to 22 carbon atoms or polyols having from 2 to 10 carbon atoms and from 2 to 6 hydroxy groups.

#### Natural or synthetic triglycerides including glyceryl esters and derivatives

Di- or tri-glycerides, based on  $C_6$ - $C_{18}$  fatty acids, modified by reaction with other alcohols (caprylic/capric triglyceride, wheat germ glycerides, etc.). Fatty acid esters of polyglycerin

(polyglyceryl-n such as polyglyceryl-4 caprate, polyglyceryl-2 isostearate, etc. or castor oil, hydrogenated vegetable oil, sweet almond oil, wheat germ oil, sesame oil, hydrogenated cottonseed oil, coconut oil, avocado oil, corn oil, hydrogenated castor oil, shea butter, cocoa butter, soybean oil, mink oil, sunflower oil, safflower oil, macadamia nut oil, olive oil, hydrogenated tallow, apricot kernel oil, hazelnut oil, borage oil, etc.

Waxes including esters of long-chain acids and alcohols as well as compounds having wax-like properties, e.g., carnauba wax, beeswax (white or yellow), lanolin wax, candelilla wax, ozokerite, japan wax, paraffin wax, microcrystalline wax, ceresin, cetearyl esters wax, synthetic beeswax etc. Also, hydrophilic waxes as cetearyl alcohol or partial glycerides.

#### Pearlescent waxes:

alkylene glycol esters, especially ethylene glycol distearate; fatty acid alkanol amides, especially coco fatty acid diethanolamide; partial glycerides, especially stearic acid monoglyceride; esters of polyvalent, unsubstituted or hydroxy-substituted carboxylic acids with fatty alcohols having from 6 to 22 carbon atoms, especially long-chained esters of tartaric acid; fatty substances, for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates, which in total have at least 24 carbon atoms, especially laurone and distearyl ether; fatty acids, such as stearic acid, hydroxystearic acid or behenic acid, ring-opening products of olefin epoxides having from 12 to 22 carbon atoms with fatty alcohols having from 12 to 22 carbon atoms and/or polyols having from 2 to 15 carbon atoms and from 2 to 10 hydroxy groups, and mixtures thereof.

#### Hydrocarbon oils:

Mineral oil (light or heavy), petrolatum (yellow or white), microcrystalline wax, paraffinic and isoparaffinic compounds, hydrogenated isoparaffinic molecules as polydecenes and polybutene, hydrogenated polyisobutene, squalane, isohexadecane, isododecane and others from plant and animal kingdom.

#### Silicones or siloxanes (organosubstituted polysiloxanes)

Dimethylpolysiloxanes, methylphenylpolysiloxanes, cyclic silicones, and also amino-, fatty acid-, alcohol-, polyether-, epoxy-, fluorine-, glycoside- and/or alkyl-modified silicone compounds, which at room temperature may be in either liquid or resinous form. Linear polysiloxanes, dimethicone (Dow Corning 200 fluid, Rhodia Mirasil DM), dimethiconol, cyclic

silicone fluids, cyclopentasiloxanes volatiles (Dow Corning 345 fluid), phenyltrimethicone (Dow Corning 556 fluid). Also suitable are simethicones, which are mixtures of dimethicones having an average chain length of from 200 to 300 dimethylsiloxane units with hydrogenated silicates. A detailed survey by Todd *et al.* of suitable volatile silicones may in addition be found in *Cosm. Toil.* 91, 27 (1976).

#### Fluorinated or perfluorinated oils

Perfluorohexane, dimethylcyclohexane, ethylcyclopentane, polyperfluoromethylisopropyl ether.

#### Emulsifiers

Any conventionally emulsifier can be used for the compositions. Emulsifier systems may comprise for example: carboxylic acids and their salts: alkaline soap of sodium, potassium and ammonium, metallic soap of calcium or magnesium, organic basis soap such as lauric, palmitic, stearic and oleic acid etc.. Alkyl phosphates or phosphoric acid esters, acid phosphate, diethanolamine phosphate, potassium cetyl phosphate. Ethoxylated carboxylic acids or polyethylene glycol esters, PEG-n acylates. Linear fatty alcohols having from 8 to 22 carbon atoms, branched from 2 to 30 mol of ethylene oxide and/or from 0 to 5 mol propylene oxide with fatty acids having from 12 to 22 carbon atoms and with alkylphenols having from 8 to 15 carbon atoms in the alkyl group. Fatty alcohol polyglycoether such as laureth-n, cetareth-n, steareth-n, oleth-n. Fatty acid polyglycoether such as PEG-n stearate, PEG-n oleate, PEG-n cocoate. Monoglycerides and polyol esters. C<sub>12</sub>-C<sub>22</sub> fatty acid mono- and di-esters of addition products of from 1 to 30 mol of ethylene oxide with polyols. Fatty acid and polyglycerol ester such as monostearate glycerol, diisostearyl polyglyceryl-3-diisostearates, polyglyceryl-3-diisostearates, triglyceryl diisostearates, polyglyceryl-2-sesquiisostearates or polyglyceryl dimerates. Mixtures of compounds from a plurality of those substance classes are also suitable. Fatty acid polyglycolesters such as monostearate diethylene glycol, fatty acid and polyethylene glycol esters, fatty acid and saccharose esters such as sucro esters, glycerol and saccharose esters such as sucro glycerides. Sorbitol and sorbitan, sorbitan mono- and di-esters of saturated and unsaturated fatty acids having from 6 to 22 carbon atoms and ethylene oxide addition products. Polysorbate-n series, sorbitan esters such as sesquiisostearate, sorbitan, PEG-(6)-isostearate sorbitan, PEG-(10)-sorbitan laurate, PEG-17- dioleate sorbitan. Glucose derivatives, C<sub>8</sub>-C<sub>22</sub> alkyl-mono and oligo-glycosides and ethoxylated analogues with glucose being preferred as the sugar component. O/W

emulsifiers such as methyl gluceth-20 sesquistearate, sorbitan stearate/sucrose cocoate, methyl glucose sesquistearate, cetearyl alcohol/cetearyl glucoside. W/O emulsifiers such as methyl glucose dioleate/ methyl glucose isostearate. Sulfates and sulfonated derivatives, dialkylsulfosuccinates, dioctyl succinate, alkyl lauryl sulfonate, linear sulfonated paraffins, sulfonated tetrapropylene sulfonate, sodium lauryl sulfates, ammonium and ethanolamine lauryl sulfates, lauryl ether sulfates, sodium laureth sulfates, sulfosuccinates, acetyl isothionates, alkanolamide sulfates, taurines, methyl taurines, imidazole sulfates. Amine derivatives, amine salts, ethoxylated amines, oxide amine with chains containing an heterocycle such as alkyl imidazolines, pyridine derivatives, isoquinoteines, cetyl pyridinium chloride, cetyl pyridinium bromide, quaternary ammonium such as cetyltrimethylbromide ammonium bromide (CTBA), stearylalkonium. Amide derivatives, alkanolamides such as acylamide DEA, ethoxylated amides such as PEG-n acylamide, oxydeamide. Poly-siloxane/polyalkyl/polyether copolymers and derivatives, dimethicone, copolyols, silicone polyethylene oxide copolymer, silicone glycol copolymer. Propoxylated or POE-n ethers (Meroxapols), Polaxamers or poly(oxyethylene)m-block-poly(oxypropylene)n-block(oxyethylene). Zwitterionic surfactants that carry at least one quaternary ammonium group and at least one carboxylate and/or sulfonate group in the molecule. Zwitterionic surfactants that are especially suitable are betaines, such as N-alkyl-N,N-dimethylammonium glycinate, cocoalkyldimethylammonium glycinate, N-acylaminopropyl-N,N-dimethylammonium glycinate, cocoacylaminopropyldimethylammonium glycinate and 2-alkyl-3-carboxymethyl-3-hydroxyethylimidazolines each having from 8 to 18 carbon atoms in the alkyl or acyl group and also cocoacylaminoethylhydroxyethylcarboxymethylglycinate, N-alkylbetaine, N-alkylaminobetaines. Alkylimidazolines, alkylpeptides, lipoaminoacids, self emulsifying bases and the compounds as described in K.F.DePolo, A short textbook of cosmetology, Chapter 8, Table 8-7, p250-251.

Non ionic bases such as PEG-6 beeswax (and) PEG-6 stearate (and) polyglyceryl -2-iso-stearate [Apifac], glyceryl stearate ( and) PEG-100 stearate. [Arlacel 165], PEG-5 glyceryl stearate [arlatone 983 S], sorbitan oleate (and) polyglyceryl-3 ricinoleate.[Arlacel 1689], sorbitan stearate and sucrose cocoate [arlatone 2121], glyceryl stearate and laureth-23 [Cerasynth 945], cetearyl alcohol and ceteth-20 [Cetomacrogol Wax], cetearyl alcohol and polysorbate 60 and PEG-150 and stearate-20[Polawax GP 200, Polawax NF], cetearyl alcohol and cetearyl polyglucoside [Emulgade PL 1618], cetearyl alcohol and ceteareth-20 [Emulgade 1000NI, Cosmowax], cetearyl alcohol and PEG-40 castor oil [Emulgade F

Special], cetearyl alcohol and PEG-40 castor oil and sodium cetearyl sulfate [Emulgade F], stearyl alcohol and steareth-7 and steareth-10 [Emulgator E 2155], cetearyl alcohol and steareth-7 and steareth-10 [Emulsifying wax U.S.N.F], glyceryl stearate and PEG-75 stearate [Gelot 64], propylene glycol ceteth-3 acetate [Hetester PCS], propylene glycol isoceth-3 acetate [Hetester PHA], cetearyl alcohol and ceteth-12 and oleth-12 [Lanbritol Wax N 21], PEG-6 stearate and PEG-32 stearate [Tefose 1500], PEG-6 stearate and ceteth-20 and steareth-20 [Tefose 2000], PEG-6 stearate and ceteth-20 and glyceryl stearate and steareth-20 [Tefose 2561], glyceryl stearate and ceteareth-20 [Teginacid H, C, X].

Anionic alkaline bases such as PEG-2 stearate SE, glyceryl stearate SE [Monelgine, Cutina KD], propylene glycol stearate [Tegin P]. Anionic acid bases such as cetearyl Alcohol and Sodium cetearyl sulfate [Lanette N, Cutina LE, Crodacol GP], cetearyl alcohol and sodium lauryl sulfate [Lanette W], trilaneth-4 phosphate and glycol stearate and PEG-2 stearate [Sedefos 75], glyceryl stearate and sodium lauryl sulfate [Teginacid Special]. Cationic acid bases such as cetearyl alcohol and cetrimonium bromide.

The emulsifiers may be used in an amount of, for example, from 1 to 30 % by weight, especially from 4 to 20 % by weight and preferably from 5 to 10 % by weight, based on the total weight of the composition.

When formulated in O/W emulsions, the preferred amount of such emulsifier system could represent 5% to 20% of the oil phase.

#### Adjuvants and additives

The cosmetic / pharmaceutical preparations, for example creams, gels, lotions, alcoholic and aqueous/alcoholic solutions, emulsions, wax/fat compositions, stick preparations, powders or ointments, may in addition contain, as further adjuvants and additives, mild surfactants, super-fatting agents, consistency regulators, thickeners, polymers, stabilisers, biogenic active ingredients, deodorising active ingredients, anti-dandruff agents, film formers, swelling agents, further UV light-protective factors, antioxidants, hydrotropic agents, preservatives, insect repellents, self-tanning agents, solubilisers, perfume oils, colourants, bacteria-inhibiting agents and the like.

### Super-fatting agents

Substances suitable for use as super-fatting agents are, for example, lanolin and lecithin and also polyethoxylated or acrylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty acid alkanolamides, the latter simultaneously acting as foam stabilisers.

### Surfactants

Examples of suitable mild surfactants, that is to say surfactants especially well tolerated by the skin, include fatty alcohol polyglycol ether sulfates, monoglyceride sulfates, mono- and/or di-alkyl sulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid tauroids, fatty acid glutamates,  $\alpha$ -olefin sulfonates, ethercarboxylic acids, alkyl oligoglucosides, fatty acid glucamides, alkylamidobetaines and/or protein fatty acid condensation products, the latter preferably being based on wheat proteins.

### Consistency regulators/thickeners and rheology modifiers

Silicon dioxide, magnesium silicates, aluminium silicates, polysaccharides or derivatives thereof for example hyaluronic acid, xanthan gum, guar-guar, agar-agar, alginates, carrageenan, gellan, pectins, or modified cellulose such as hydroxycellulose, hydroxypropyl-methylcellulose. In addition polyacrylates or homopolymers of reticulated acrylic acids and polyacrylamides, carbomer (carbopol types 980, 981, 1382, ETD 2001, ETD2020, Ultrez 10) or Salcare range such as Salcare SC80(steareth-10 allyl ether/acrylates copolymer), Salcare SC81(acrylates copolymer), Salcare SC91 and Salcare AST(sodium acrylates copolymer/PPG-1 trideceth-6), sepiigel 305(polyacrylamide/laureth-7), Simulgel NS and Simulgel EG (hydroxyethyl acrylate / sodium acryloyldimethyl taurate copolymer), Stabilen 30 (acrylates / vinyl isodecanoate crosspolymer), Pemulen TR-1(acrylates / C10-30 alkyl acrylate crosspolymer), Luvigel EM (sodium acrylates copolymer), Aculyn 28 (acrylates/beheneth-25 methacrylate copolymer), etc..

### Polymers

Suitable cationic polymers are, for example, cationic cellulose derivatives, for example a quaternised hydroxymethyl cellulose obtainable under the name Polymer JR 400 from Amerchol, cationic starches, copolymers of diallylammonium salts and acrylamides, quaternised vinylpyrrolidone/vinyl imidazole polymers, for example Luviquat® (BASF), condensation products of polyglycols and amines, quaternised collagen polypeptides, for example lauryl-

dimonium hydroxypropyl hydrolyzed collagen (Lamequat®L/Grünau), quaternised wheat polypeptides, polyethyleneimine, cationic silicone polymers, for example amidomethicones, copolymers of adipic acid and dimethylaminohydroxypropyldiethylenetriamine (Cartaretin/Sandoz), copolymers of acrylic acid with dimethyldiallylammonium chloride (Merquat 550/Chemvicon), polyaminopolyamides, as described, for example, in FR-A-2 252 840, and the cross-linked water-soluble polymers thereof, cationic chitin derivatives, for example of quaternised chitosan, optionally distributed as microcrystals; condensation products of dihaloalkyls, for example dibromobutane, with bisdialkylamines, for example bisdimethylamino-1,3-propane, cationic guar gum, for example Jaguar C-17, Jaguar C-16 from Celanese, quaternised ammonium salt polymers, for example Mirapol A-15, Mirapol AD-1, Mirapol AZ-1 from Miranol. As anionic, zwitterionic, amphoteric and non-ionic polymers there come into consideration, for example, vinyl acetate / crotonic acid copolymers, vinylpyrrolidone / vinyl acrylate copolymers, vinyl acetate / butyl maleate / isobornyl acrylate copolymers, methyl vinyl ether / maleic anhydride copolymers and esters thereof, uncrosslinked polyacrylic acids and polyacrylic acids crosslinked with polyols, acrylamidopropyl-trimethylammonium chloride /acrylate copolymers, octyl acrylamide/methyl methacrylate/tert-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers, polyvinylpyrrolidone, vinylpyrrolidone/-vinyl acetate copolymers, vinylpyrrolidone/dimethylaminoethyl methacrylate/vinyl caprolactam terpolymers and also optionally derivatised cellulose ethers and silicones. Furthermore the polymers as described in EP 1093796 (pages 3-8, paragraphs 17-68) may be used.

#### Biogenic active ingredients

Biogenic active ingredients are to be understood as meaning, for example, tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid, deoxyribonucleic acid, retinol, bisabolol, allantoin, phytantriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides, essential oils, plant extracts and vitamin complexes.

#### Deodorising active ingredients

As deodorising active ingredients there come into consideration, for example, antiperspirants, for example aluminium chlorohydrates (see J. Soc. Cosm. Chem. 24, 281 (1973)). Under the trade mark Locron® of Hoechst AG, Frankfurt (FRG), there is available commercially, for example, an aluminium chlorohydrate corresponding to formula  $\text{Al}_2(\text{OH})_5\text{Cl} \times 2.5 \text{ H}_2\text{O}$ , the use of which is especially preferred (see J. Pharm. Pharmacol. 26,



531 (1975)). Besides the chlorohydrates, it is also possible to use aluminium hydroxyacetates and acidic aluminium/zirconium salts. Esterase inhibitors may be added as further deodorising active ingredients. Such inhibitors are preferably trialkyl citrates, such as trimethyl citrate, tripropyl citrate, triisopropyl citrate, tributyl citrate and especially triethyl citrate (Hydagen CAT, Henkel), which inhibit enzyme activity and hence reduce odour formation. Further substances that come into consideration as esterase inhibitors are sterol sulfates or phosphates, for example lanosterol, cholesterol, campesterol, stigmasterol and sitosterol sulfate or phosphate, dicarboxylic acids and esters thereof, for example glutaric acid, glutaric acid monoethyl ester, glutaric acid diethyl ester, adipic acid, adipic acid monoethyl ester, adipic acid diethyl ester, malonic acid and malonic acid diethyl ester and hydroxycarboxylic acids and esters thereof, for example citric acid, malic acid, tartaric acid or tartaric acid diethyl ester. Antibacterial active ingredients that influence the germ flora and kill or inhibit the growth of sweat-decomposing bacteria can likewise be present in the preparations (especially in stick preparations). Examples include chitosan, phenoxyethanol and chlorhexidine gluconate. 5-chloro-2-(2,4-dichlorophenoxy)-phenol (Triclosan, Irgasan, Ciba Specialty Chemicals Inc.) has also proved especially effective.

#### Anti-dandruff agents

As anti-dandruff agents there may be used, for example, climbazole, octopirox and zinc pyri-thione.

#### Film formers

Customary film formers include, for example, chitosan, microcrystalline chitosan, quaternised chitosan, polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymers, polymers of quaternary cellulose derivatives containing a high proportion of acrylic acid, collagen, hyaluronic acid and salts thereof and similar compounds.

#### Antioxidants

In addition to the primary light-protective substances it is also possible to use secondary light-protective substances of the antioxidant kind that interrupt the photochemical reaction chain triggered when UV radiation penetrates the skin or hair. Typical examples of such anti-oxidants are amino acids (e.g. glycine, histidine, tyrosine, tryptophan) and derivatives thereof, imidazoles (e.g. urocanic acid) and derivatives thereof, peptides, such as D,L-carnosine, D-carnosine, L-carnosine and derivatives thereof (e.g. anserine), carotinoids, carotenes,

lycopene and derivatives thereof, chlorogenic acid and derivatives thereof, lipoic acid and derivatives thereof (e.g. dihydrolipoic acid), aurothioglycose, propylthiouracil and other thiols (e.g. thioredoxin, glutathione, cysteine, cystine, cystamine and the glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl, lauryl, palmitoyl, oleyl, linoleyl, cholesteryl and glyceryl esters thereof) and also salts thereof, dilauryl thiodipropionate, distearyl thiodipropionate, thiodipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and also sulfoximine compounds (e.g. buthionine sulfoximines, homocysteine sulfoximine, buthionine sulfones, penta-, hexa-, hepta-thionine sulfoximine), also (metal) chelating agents (e.g. hydroxy fatty acids, palmitic acid phytic acid, lactoferrin), hydroxy acids (e.g. citric acid, lactic acid, malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EDDS, EGTA and derivatives thereof, unsaturated fatty acids and derivatives thereof (e.g. linolenic acid, linoleic acid, oleic acid), folic acid and derivatives thereof, ubiquinone and ubiquinol and derivatives thereof, vitamin C and derivatives (e.g. ascorbyl palmitate, magnesium ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (e.g. vitamin E acetate), vitamin A and derivatives (e.g. vitamin A palmitate) and also coniferyl benzoate of benzoin resin, rutinic acid and derivatives thereof, glycosylrutin, ferulic acid, furfurylidene glucitol, carnosine, butyl hydroxytoluene, butyl hydroxyanisole, nordihydroguaiaretic acid, trihydroxybutyrophenone, uric acid and derivatives thereof, mannose and derivatives thereof, superoxide dismutase, N-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]sulfanilic acid (and salts thereof, for example the disodium salts), zinc and derivatives thereof (e.g. ZnO, ZnSO<sub>4</sub>), selenium and derivatives thereof (e.g. selenium methionine), stilbene and derivatives thereof (e.g. stilbene oxide, trans-stilbene oxide) and the derivatives suitable according to the invention (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids) of those mentioned active ingredients. HALS ("Hindered Amine Light Stabilizers") compounds may also be mentioned. The amount of antioxidants present is usually from 0.001 to 30 % by weight, preferably from 0.01 to 3 % by weight, based on the weight of the UV absorber of formula (1).

#### Hydrotropic agents

To improve the flow behaviour it is also possible to employ hydrotropic agents, for example ethoxylated or non ethoxylated mono-alcohols, diols or polyols with a low number of carbon atoms or their ethers (e.g. ethanol, isopropanol, 1,2-dipropenediol, propylene glycol, glycerine, ethylene glycol, ethylene glycol monoethyl ether, ethylene glycol monobutylether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol

monobutyl ether, diethylene glycol monomethyl ether; diethylene glycol monoethyl ether, diethylene glycol monobutyl ether and similar products). The polyols that come into consideration for that purpose have preferably from 2 to 15 carbon atoms and at least two hydroxy groups. The polyols may also contain further functional groups, especially amino groups, and/or may be modified with nitrogen. Typical examples are as follows: glycerol, alkylene glycols, for example ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol and also polyethylene glycols having an average molecular weight of from 100 to 1000 Dalton; technical oligoglycerol mixtures having an intrinsic degree of condensation of from 1.5 to 10, for example technical diglycerol mixtures having a diglycerol content of from 40 to 50 % by weight; methylol compounds, such as, especially, trimethylolethane, trimethylolpropane, trimethylolbutane, pentaerythritol and dipentaerythritol; lower alkyl-glucosides, especially those having from 1 to 8 carbon atoms in the alkyl radical, for example methyl and butyl glucoside; sugar alcohols having from 5 to 12 carbon atoms, for example sorbitol or mannitol; sugars having from 5 to 12 carbon atoms, for example glucose or saccharose; amino sugars, for example glucamine; dialcohol amines, such as diethanolamine or 2-amino-1,3-propanediol.

#### Preservatives

Suitable preservatives include, for example, methyl-, ethyl-, propyl-, butyl- parabens, benzalconium chloride, 2-Bromo-2-nitro-propane-1,3-diol, dehydroacetic acid, diazolidinyl Urea, 2-dichloro-benzyl alcohol, DMDM hydantoin, formaldehyde solution, methyldibromoglutanitrile, phenoxyethanol, Sodium hydroxymethylglycinate, imidazolidinyl urea, Triclosan and further substance classes listed in the following reference: K.F.DePolo –A short textbook of cosmetology, Chapter 7, Table 7-2, 7-3, 7-4 and 7-5, p210-219.

#### Bacteria-inhibiting agents

Typical examples of bacteria-inhibiting agents are preservatives that have a specific action against gram-positive bacteria, such as 2,4,4'-trichloro-2'-hydroxydiphenyl ether, chlorhexidine (1,6-di(4-chlorophenyl-biguanido)hexane) or TCC (3,4,4'-trichlorocarbanilide). A large number of aromatic substances and ethereal oils also have antimicrobial properties. Typical examples are the active ingredients eugenol, menthol and thymol in clove oil, mint oil and thyme oil. A natural deodorising agent of interest is the terpene alcohol farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol), which is present in lime blossom oil. Glycerol monodaurate has also proved to be a bacteriostatic agent. The amount of the additional bacteria-inhibiting

agents present is usually from 0.1 to 2 % by weight, based on the solids content of the preparations.

### Perfume oils

There may be mentioned as perfume oils mixtures of natural and/or synthetic aromatic substances. Natural aromatic substances are, for example, extracts from blossom (lilies, lavender, roses, jasmine, neroli, ylang-ylang), from stems and leaves (geranium, patchouli, petit-grain), from fruit (aniseed, coriander, caraway, juniper), from fruit peel (bergamot, lemons, oranges), from roots (mace, angelica, celery, cardamom, costus, iris, calmus), from wood (pinewood, sandalwood, guaiacum wood, cedarwood, rosewood), from herbs and grasses (tarragon, lemon grass, sage, thyme), from needles and twigs (spruce, pine, Scots pine, mountain pine), from resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opoponax). Animal raw materials also come into consideration, for example civet and castoreum. Typical synthetic aromatic substances are, for example, products of the ester, ether, aldehyde, ketone, alcohol or hydrocarbon type. Aromatic substance compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert-butylcyclohexyl acetate, linalyl acetate, dimethylbenzylcarbonyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethylmethylphenyl glycinate, allylcyclohexyl propionate, styryl propionate and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals having from 8 to 18 hydrocarbon atoms, citral, citronellal, citronellyl oxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilyal and bourgeonal; the ketones include, for example, the ionones, isomethylionone and methyl cedryl ketone; the alcohols include, for example, anethol, citronellol, eugenol, isoeugenol, geraniol, linalool, phenyl ethyl alcohol and terpinol; and the hydrocarbons include mainly the terpenes and balsams. It is preferable, however, to use mixtures of various aromatic substances that together produce an attractive scent. Ethereal oils of relatively low volatility, which are chiefly used as aroma components, are also suitable as perfume oils, e.g. sage oil, camomile oil, clove oil, melissa oil, oil of cinnamon leaves, lime blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil, labolanum oil and lavandin oil. Preference is given to the use of bergamot oil, dihydromyrcenol, lilyal, lyral, citronellol, phenyl ethyl alcohol, hexyl cinnamaldehyde, geraniol, benzyl acetone, cyclamen aldehyde, linalool, boisambrene forte, ambroxan, indole, hedione, sandelice, lemon oil, tangerine oil, orange oil, allyl amyl glycolate, cyclovertal, lavandin oil, muscatel sage oil, damascone, bourbon geranium oil, cyclohexyl salicylate, vertofix coeur,

iso-E-Super, Fixolide NP, evernyl, iraldein gamma, phenylacetic acid, geranyl acetate, benzyl acetate, rose oxide, romillat, irotyl and floramat alone or in admixture with one another.

#### Colourants

There may be used as colourants the substances that are suitable and permitted for cosmetic purposes, as compiled, for example, in the publication "Kosmetische Färbemittel" of the Farbstoffkommission der Deutschen Forschungsgemeinschaft, Verlag Chemie, Weinheim, 1984, pages 81 to 106. The colourants are usually used in concentrations of from 0.001 to 0.1 % by weight, based on the total mixture.

#### Other adjuvants

It is furthermore possible for the cosmetic preparations to contain, as adjuvants, anti-foams, such as silicones, *structurants*, such as maleic acid, *solubilisers*, such as ethylene glycol, propylene glycol, glycerol or diethylene glycol, opacifiers, such as latex, styrene/PVP or styrene/acrylamide copolymers, complexing agents, such as EDTA, NTA, alaninediacetic acid or phosphonic acids, *propellants*, such as propane/butane mixtures, N<sub>2</sub>O, dimethyl ether, CO<sub>2</sub>, N<sub>2</sub> or air, so-called coupler and developer components as oxidation dye precursors, *reducing agents*, such as thioglycolic acid and derivatives thereof, thiolactic acid, cysteamine, thiomalic acid or mercaptoethanesulfonic acid, or oxidising agents, such as hydrogen peroxide, potassium bromate or sodium bromate.

Suitable insect repellents are, for example, N,N-diethyl-m-toluamide, 1,2-pentanediol or insect repellent 3535; suitable self-tanning agents are, for example, dihydroxyacetone and/or erythrulose or dihydroxy acetone and/or dihydroxy acetone precursors as described in WO 01/85124 and/or erythrulose.

#### Polymeric beads or hollow spheres as SPF enhancers

The combination of the UV-absorbers and UV-absorber combinations, listed above, with SPF enhancers, such as non-active ingredients like Styrene/acrylates copolymer, silica beads, spheroidal magnesium silicate, crosslinked Polymethylmethacrylates (PMMA ; Micoppearl M305 Seppic), can maximize better the UV protection of the sun products. Holosphere additives (Sunspheres® ISP, Silica Shells Kobo.) deflect radiation and the effective path length of the photon is therefore increased. (EP0893119). Some beads, as mentioned previously, provide a soft feel during spreading. Moreover, the optical activity of such beads,

e.g. Micropearl M305, can modulate skin shine by eliminating reflection phenomena and indirectly may scatter the UV light. When formulated in O/W emulsions, the preferably amount of such SPF enhancers should represent 1% to 10% of the total amount of the emulsion.

#### Cosmetic or pharmaceutical preparations

Cosmetic or pharmaceutical formulations are contained in a wide variety of cosmetic preparations. There come into consideration, for example, especially the following preparations:

- skin-care preparations, e.g. skin-washing and cleansing preparations in the form of tablet-form or liquid soaps, soapless detergents or washing pastes,
- bath preparations, e.g. liquid (foam baths, milks, shower preparations) or solid bath preparations, e.g. bath cubes and bath salts;
- skin-care preparations, e.g. skin emulsions, multi-emulsions or skin oils;
- cosmetic personal care preparations, e.g. facial make-up in the form of day creams or powder creams, face powder (loose or pressed), rouge or cream make-up, eye-care preparations, e.g. eyeshadow preparations, mascara, eyeliner, eye creams or eye-fix creams; lip-care preparations, e.g. lipsticks, lip gloss, lip contour pencils, nail-care preparations, such as nail varnish, nail varnish removers, nail hardeners or cuticle removers;
- foot-care preparations, e.g. foot baths, foot powders, foot creams or foot balsams, special deodorants and antiperspirants or callus-removing preparations;
- light-protective preparations, such as sun milks, lotions, creams or oils, sunblocks or tropicals, pre-tanning preparations or after-sun preparations;
- skin-tanning preparations, e.g. self-tanning creams;
- depigmenting preparations, e.g. preparations for bleaching the skin or skin-lightening preparations;
- insect-repellents, e.g. insect-repellent oils, lotions, sprays or sticks;
- deodorants, such as deodorant sprays, pump-action sprays, deodorant gels, sticks or roll-ons;
- antiperspirants, e.g. antiperspirant sticks, creams or roll-ons;
- preparations for cleansing and caring for blemished skin, e.g. synthetic detergents (solid or liquid), peeling or scrub preparations or peeling masks;

- hair-removal preparations in chemical form (depilation), e.g. hair-removing powders, liquid hair-removing preparations, cream- or paste-form hair-removing preparations, hair-removing preparations in gel form or aerosol foams;
- shaving preparations, e.g. shaving soap, foaming shaving creams, non-foaming shaving creams, foams and gels, preshave preparations for dry shaving, aftershaves or aftershave lotions;
- fragrance preparations, e.g. fragrances (eau de Cologne, eau de toilette, eau de parfum, parfum de toilette, perfume), perfume oils or perfume creams;
- cosmetic hair-treatment preparations, e.g. hair-washing preparations in the form of shampoos and conditioners, hair-care preparations, e.g. pretreatment preparations, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-structuring preparations, e.g. hair-waving preparations for permanent waves (hot wave, mild wave, cold wave), hair-straightening preparations, liquid hair-setting preparations, hair foams, hairsprays, bleaching preparations, e.g. hydrogen peroxide solutions, lightening shampoos, bleaching creams, bleaching powders, bleaching pastes or oils, temporary, semi-permanent or permanent hair colourants, preparations containing self-oxidising dyes, or natural hair colourants, such as henna or camomile.

#### Presentation forms

The final formulations listed may exist in a wide variety of presentation forms, for example:

- in the form of liquid preparations as a W/O, O/W, O/W/O, W/O/W or PIT emulsion and all kinds of microemulsions,
- in the form of a gel,
- in the form of an oil, a cream, milk or lotion,
- in the form of a powder, a lacquer, a tablet or make-up,
- in the form of a stick,
- in the form of a spray (spray with propellant gas or pump-action spray) or an aerosol,
- in the form of a foam, or
- in the form of a paste.

Of special importance as cosmetic preparations for the skin are light-protective preparations, such as sun milks, lotions, creams, oils, sunblocks or tropicals, pretanning preparations or

after-sun preparations, also skin-tanning preparations, for example self-tanning creams. Of particular interest are sun protection creams, sun protection lotions, sun protection milk and sun protection preparations in the form of a spray.

Of special importance as cosmetic preparations for the hair are the above-mentioned preparations for hair treatment, especially hair-washing preparations in the form of shampoos, hair conditioners, hair-care preparations, e.g. pretreatment preparations, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-straightening preparations, liquid hair-setting preparations, hair foams and hairsprays. Of special interest are hair-washing preparations in the form of shampoos.

A shampoo has, for example, the following composition: from 0.01 to 5 % by weight of a UV absorber according to the invention, 12.0 % by weight of sodium laureth-2-sulfate, 4.0 % by weight of cocamidopropyl betaine, 3.0 % by weight of sodium chloride, and water ad 100%.

For example, especially the following hair-cosmetic formulations may be used:

- a<sub>1</sub>) spontaneously emulsifying stock formulation, consisting of the UV absorber according to the invention, PEG-6-C<sub>10</sub>oxoalcohol and sorbitan sesquioleate, to which water and any desired quaternary ammonium compound, for example 4 % minkamidopropyl dimethyl-2-hydroxyethylammonium chloride or Quaternium 80 is added;
- a<sub>2</sub>) spontaneously emulsifying stock formulation consisting of the UV absorber according to the invention, tributyl citrate and PEG-20-sorbitan monooleate, to which water and any desired quaternary ammonium compound, for example 4 % minkamidopropyl dimethyl-2-hydroxyethylammonium chloride or Quaternium 80 is added;
- b) quat-doped solutions of the UV absorber according to the invention in butyl triglycol and tributyl citrate;
- c) mixtures or solutions of the UV absorber according to the invention with n-alkylpyrrolidone.

Other typical ingredients in such formulations are preservatives, bactericides and bacteriostatic agents, perfumes, dyes, pigments, thickening agents, moisturizing agents, humectants, fats, oils, waxes or other typical ingredients of cosmetic and personal care formulations such as alcohols, poly-alcohols, polymers, electrolytes, organic solvents, silicon derivatives,



emollients, emulsifiers or emulsifying surfactants, surfactants, dispersing agents, antioxidants, anti-irritants and anti-inflammatory agents etc.

Examples of cosmetic and pharmaceutical preparations (X = preferred combinations)

O/W systems:

Ingredients	1	2	3	4	5	6	7	8
<b>Emulsifiers</b>								
Potassium Cetyl Phosphate 2%-5%	X							
Cetearyl Alcohol/ Dicetyl Phosphate/Ceteth-10 Phosphate 2%-6%		X						
Sodium Stearyl Phtalamate 1%-2%			X					
Cetearyl Alcohol/Behentrimonium Methosulfate 1%-5%				X				
Quaternium-32 1%-5%					X			
Dimethicone copolyol/ Caprylic/Capric Triglyceride 1%-4%						X		
Steareth-2 /Steareth-21 2%-5%							X	
Polyglyceryl Methyl Glucose Distearate 1%-4%								X
Lipophilic emollient/dispersant oil 15%-20%	X	X	X	X	X	X	X	X
Fatty Alcohols and/or Waxes 1%-5%	X	X	X	X	X	X	X	X
Thickeners (water swellable thickeners) 0.5% - 1.5%	X	X	X	X	X	X	X	X
Preservatives 0.5% - 1%	X	X	X	X	X	X	X	X
Chelating agents (such as EDTA) 0%-0.2%	X	X	X	X	X	X	X	X
Antioxidants 0.05% - 0.2%	X	X	X	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X	X	X	X
Perfume oils 0.1% - 0.4%	X	X	X	X	X	X	X	X
UV-absorber according to the invention 1% - 20%	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0% - 30%	X	X	X	X	X	X	X	X

W/O systems

Ingredients	1	2	3	4	5
<b>Emulsifiers</b>	X	X	X	X	X
Polyglyceryl-2 Dipolyhydroxystearate 2%-4%	X	X	X	X	X
PEG-30 Dipolyhydroxystearate 2%-4%		XX			
Rapeseed Oil Sorbitol Esters 1%-5%			X X		
PEG-45/Dodecyl Glycol Copolymer 1%-5%				X	
Sorbitan Oleate / Polycerol-3 ricinoleate 1%-5%					X
Lipophilic emollient/dispersant oil 10% - 20%	X	X	X	X	X
Fatty Alcohols and/or Waxes 10% - 15%	X	X	X	X	X
Electrolytes (NaCl, MgSO <sub>4</sub> ) 0.5% - 1%	X	X	X	X	X
Polyol phase (Propylene glycol, glycerin) 1% - 8%	X	X	X	X	X
Preservatives 0.3% - 0.8%	X	X	X	X	X

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<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Perfume oils 0.1% - 0.4%	X	X	X	X	X
Chelating agents (such as EDTA) 0% - 0.2%	X	X	X	X	X
Antioxidants 0.05% - 0.2%	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X
UV-absorber according to the invention 1% - 20%.	X	X	X	X	X
UV-absorber as described in table 1-3 0% - 30%.	X	X	X	X	X

W/Silicone systems

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
<u>Emulsifiers</u>				
Dimethicone Copolyol / Cyclomethicone 5%-10%	X		X	
Laurylmethicone Copolyol 5%-10%		X		X
<u>Silicone phase</u>				
Cyclopentasiloxane 15%-25%	X			X
Dimethicone 15%-25%		X	X	
<u>Silicone elastomer</u>				
Dimethicone/Vinyldimethicone Crosspolymer 1%-10%	X	X	X	X
Humectant/polyols (Propylene glycol, glycerin...) 2%-8%	X	X	X	X
Chelating agents (such as EDTA) 0%-0.2%	X	X	X	X
Antioxidants 0.05%-0.2%	X	X	X	X
Preservatives 0.3%-0.8%	X	X	X	X
Perfume oils 0.1%-0.4%	X	X	X	X
Water deionized Qs 100%	X	X	X	X
UV-absorber according to the invention 1% - 20%	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X

Multiple emulsions

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
<u>Primary emulsion W1/O</u>												
PEG-30 Dipolyhydroxystearate 2%-6%	X									X		X
Cetyl Dimethicone Copolyol 1%-3%		X							X			
PEG-30 Dipolyhydroxystearate/ Steareth-2/ Steareth-21 4%-6%			X					X				
Polyglyceryl-2 Dipolyhydroxystearate 1%-3%				X			X					
Polyglyceryl-6 Ricinoleate 1%-3%					X	X					X	
<u>Oil phase 15%-30%</u>												
Fatty acid esters	X	X	X	X	X						X	X
Natural and synthetic Triglycerides						X	X	X	X	X	X	X
Hydrocarbon oils	X	X	X	X	X						X	X
Silicone oils						X	X	X	X	X	X	X

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
Preservatives 0.3% - 0.8%	X	X	X	X	X	X	X	X	X	X	X	X
Water Deioniz. qs 100%	X	X	X	X	X	X	X	X	X	X	X	X
Ionic monofunctional O/W emulsifiers												
Sorbitan Stearate/Sucrose Cocoate 3% - 7%	X							X				X
Sucrose Laurate 3%-7%		X					X				X	
Poloxamer 407 3%-7%			X			X			X			
Polyoxyethylene(20)Sorbate Monooleate 3%-5%				X	X					X		
Primary emulsion W1/O 50%	X	X	X	X	X	X	X	X	X	X	X	X
Thickeners (water swellable polymers) 0.3%-1%	X	X	X	X	X	X	X	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X	X	X	X	X	X	X	X
Perfume oils 0.1%-0.4%	X	X	X	X	X	X	X	X	X	X	X	X
UV-absorber according to the invention 1%-20%	X	X	X	X	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0% - 30%	X	X	X	X	X	X	X	X	X	X	X	X

O1/W/O2 emulsions

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
Primary emulsion O1/W								
PEG-60 Hydrogenated Castor Oil 25%	X			X	X			X
Steareth-25 25%		X	X			X	X	
Oil phase 75%								
Fatty acid esters	X		X					
Natural and synthetic Triglycerides		X		X				
Hydrocarbon oils					X		X	
Silicone oils						X		X
Preservatives 0.3% - 0.8%	X	X	X	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X	X	X	X
Non ionic multifunctional W/O emulsifier 2%-5%	X	X	X	X	X	X	X	X
Waxes 1%-5%	X	X	X	X	X	X	X	X
Oil phase 20%-30%	X	X	X	X	X	X	X	X
Fatty acid esters								
Natural and synthetic Triglycerides								
Hydrocarbon oils								
Silicone oils								
Primary emulsion O1/W 15%	X	X	X	X	X	X	X	X
Electrolytes (NaCl, MgSO <sub>4</sub> ) 0.1%-0.5%	X	X	X	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X	X	X	X
Perfume oils 0.1%-0.4%	X	X	X	X	X	X	X	X
UV-absorber according to the invention 1%-20%	X	X	X	X	X	X	X	X

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
UV-absorber as described in table 1-3 0%-30%	X	X	X	X	X	X	X	X

Microemulsions

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
Surfactants										
PEG-8 Caprylic/Capric Glycerides 10%-25%	X			X	X			X	X	
PPG-5-ceteth-20 10%-25%		X	X			X	X			X
Co-surfactants										
Polyglyceryl-6 Isostearate 5%-15%	X		X							
Polyglyceryl-3 Diisostearate 5%-15%		X		X						
Polyglyceryl-6 Dioleate 5%-15%					X		X			
PPG-10 Cetyl Ether 5%-15%						X		X		
Ethoxydiglycol 5%-15%									X	X
Oil phase 10%-80%	X	X	X	X	X	X	X	X	X	X
Isostearyl Benzoate										
Isostearyl Isostearate										
PEG-7 Glyceryl Cocoate										
Cyclomethicone										
Polyalcohols/Humectants 1%-10%	X	X	X	X	X	X	X	X	X	X
Preservatives 0.3 -0.8%	X	X	X	X	X	X	X	X	X	X
Perfume oils 0.1%-0.4%	X	X	X	X	X	X	X	X	X	X
Water Deioniz. qs 100%	X	X	X	X	X	X	X	X	X	X
UV-absorber according to the invention 1%-20%	X	X	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X	X	X	X	X	X	X

O/W Spray emulsions

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Emulsifiers						
Alkyl Phosphates 0.1%-5%	X			X	X	
Glucosidic derivatives 0.1%-5%		X	X			X
Solubilisants						
Ethoxylated Glyceryl ethers 0.1%-1%	X		X			
Polysorbates 0.1%-1%		X		X		
Ethoxylated Oleyl ethers 0.1%-1%					X	X
Film forming agents						
PVP/VA Copolymer 1%-10%	X		X		X	
PVM/MA Copolymer 1%-10%		X		X		X
Oil phase 5%-20%	X	X	X	X	X	X
Natural oils(Meadowfoam, Jojoba, Macadamia...)						
Fatty acids esters						
Mineral oils						

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Silicone oils						
Alcohol 0%-50%	X	X	X	X	X	X
Thickeners 0.1%-0.5%	X	X	X	X	X	X
Polyacrylates						
Aluminium/Magnesium Silicates						
Gums						
Neutralizing agents 0%-1%	X	X	X	X	X	X
Polyalcohols/Humectants 1%-5%	X	X	X	X	X	X
Chelating agents (such as EDTA) 0%-0.2%	X	X	X	X	X	X
Antioxidants 0.05%-0.2%	X	X	X	X	X	X
Water Deioniz. qs 100%	X	X	X	X	X	X
Perfume oils 0.1%- 0.5%	X	X	X	X	X	X
Preservatives 0.4%-1%	X	X	X	X	X	X
UV-absorber according to the invention 1% - 20%	X	X	X	X	X	X
UV-absorber as described in table 1-3 0% - 30%	X	X	X	X	X	X

### G – Aqueous

[illegible]

Oleogels

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
<u>Thickeners</u>										
Hydrogenated Lecithin 1%-10%	X									X
Silica Dimethyl Silylate 1%-10%		X							X	
Silica 1%-5%			X					X		
C <sub>24-28</sub> Alkyl Dimethicone 1%-5%				X			X			
Aluminium or Magnesium Stearate 1%-5%					X	X				
Polyols – Humectants 5%-70%	X	X	X	X	X	X	X	X	X	X
Oil phase 20% - 90%										
Dicaprylyl Ether	X					X		X		
Phenyl Trimethicone		X					X			
Hydrogenated Polyisobutene			X							
Isopropyl Isostearate				X					X	
Oleogel basis (Mineral oil and hydrogenated Butylene/Ethylene or Ethylene/Propylene Styrene Copolymer)					X					X
Silicone wax 1%-10%	X	X	X	X	X	X	X	X	X	X
Dimethiconol Behenate										
Dimethiconol Stearate										
Perfume oils 0.1%-0.5%	X	X	X	X	X	X	X	X	X	X
Antioxidants 0.05%-0.2%	X	X	X	X	X	X	X	X	X	X
UV-absorber according to the invention 1%-20%	X	X	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X	X	X	X	X	X	X

Light/dry cosmetic oils

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
<u>Lipophilic base</u>				
Hydrocarbon oils 30%-70%	X			X
Fatty acid esters branched or not 10%-50%		X	X	
<u>Light feel agent</u>				
Silicones/Siloxanes 0% - 10%	X		X	
Perfluorinated oils and Perfluoroethers 0%-10%		X		X
Viscosifying agents 0%-10%	X	X	X	X
<u>Waxes</u>				
Esters of long chain acids and alcohols 0% - 2%	X	X	X	X
Antioxidants 0.1%-1%	X	X	X	X
Solubilisants/dispersing agents 0%-5%	X	X	X	X
Perfume oils 0.1%-0.5%	X	X	X	X
UV-absorber according to the invention 1%-20%.	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X

Foaming/mousse products

<u>Ingredients</u>	
SD Alcohol 40 0%-8%	X
Propellant 8%-15%	X
Nonionic Emulsifier/Surfactant 0.5% - 3%	X
Corrosion Inhibitor 0% - 1%	X
Perfume oils 0.1% - 0.5%	X
Preservatives 0.1%-1%	X
Miscellaneous 0%-1%	X
UV-absorber according to the invention 1%-20%.	X
UV-absorber as described in table 1-3 0%-30%	X

Stick products

<u>Ingredients</u>	
Waxes 15%-30%	X
Natural and silicone oils 20%-75%	X
Lanoline derivatives 5%->50%	X
Esters of lanolin	x
Acetylated lanolin	x
Lanolin oil	x
Colorants and pigments 10% - 15%	X
Antioxidants 0.1% - 0.8%	X
Perfume oils 0.1% - 2%	X
Preservatives 0.1%-0.7%	X
UV-absorber according to the invention 1%-20% .	X
UV-absorber as described in table 1-3 0%-30%	X

Liquid and compact

<u>Ingredients</u>	<u>1</u>	<u>2</u>
<u>Liquid foundation</u>		
Powder phase 10%-15%	X	
Oil phase 30% - 40%; 75% (only for anhydrous form)	X	
Thickener/suspending agents 1%-5%	X	
Film forming polymers 1%-2%	X	
Antioxidants 0.1% - 1%	X	
Perfume oils 0.1% - 0.5%	X	
Preservatives 0.1%-0.8%	X	
Water deionized Qs 100%	X	
<u>Compact powder</u>		
Powder phase 15%-50%		X
Oil phase 15% - 50%		X

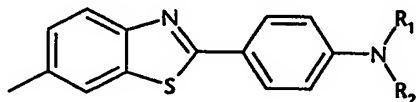
Ingredients	1	2
Polyol phase 5% - 15%		X
Antioxidants 0.1%-1%		X
Perfume oils 0.1% - 0.5%		X
Preservatives 0.1%-0.8%		X
For the two product forms		
UV-absorber according to the invention 1%-20%	X	X
UV-absorber as described in table 1-3 0%-30%	X	X

Conditioning Shampoos

Ingredients	1
Primary surfactants (listed previously) 5%-10%	X
Secondary surfactants (listed previously) 5%-15%	X
Foam Stabilizers (listed previously) 0%-5%	X
Water deionized 40%-70%	X
Actives 0 -10%	X
Conditioners	x
Refatting agents	x
Moisturizing agents	x
Thickeners/Rheology modifiers 0%-3%	X
Humectants 0 %-2%	X
pH adjusting agents 0 %-1%	X
Preservatives 0.05 %-1%	X
Perfume oils 0.1%-1%	X
Antioxidants 0.05 %-0.20%	X
Chelating Agents (EDTA) 0%-0.2%	X
Opacifying agents 0%-2%	X
UV-absorber according to the invention 1%-20%	X
UV-absorber as described in table 1-3 0%-30%	X

The cosmetic preparation according to the invention is distinguished by excellent protection of human skin against the damaging effect of sunlight.

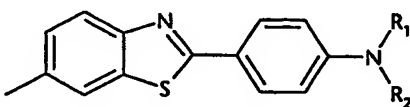

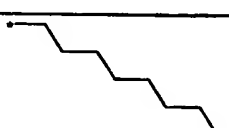


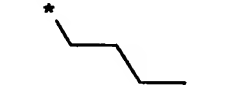
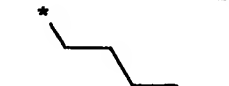
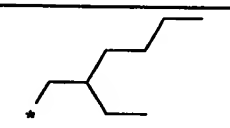
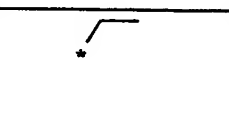


Preparation ExamplesExample 1: General work procedure for the synthesis of dialkylated compounds offormula

2-(4-Aminophenyl)-6-methylbenzothiazole (0.12 mol) is dissolved in 200 ml of absolute tetrahydrofuran and cooled to  $-10^{\circ}\text{C}$ . At from  $-5$  to  $-10^{\circ}\text{C}$ , 6.34 g of (0.264 mol) of sodium hydride is added, in portions, to the solution. The reaction mixture is stirred at  $10^{\circ}\text{C}$  for 30 minutes. Then, 0.28 mol of the appropriate haloalkane dissolved in 200 ml of absolute tetrahydrofuran is added dropwise in such a manner that the reaction temperature does not exceed  $10^{\circ}\text{C}$ . The reaction mixture is then heated to boiling point and refluxed for about 20 hours. After the reaction is complete, 10 ml of methanol are added and the reaction mixture is then reduced to half its original volume using a rotary evaporator. After adding 200 ml of distilled water, the crude product is extracted with ethyl acetate. Subsequent column chromatography over silica gel using a mixture of cyclohexane and ethyl acetate yields the pure product, which is dried under a high vacuum at  $80^{\circ}\text{C}$  and 0.02 mbar.

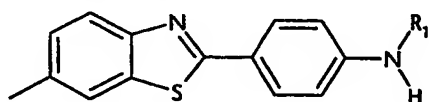
The following compounds may be prepared by this method:

	<u>General formula</u>		
<u>Comp. of formula</u>	<u>R<sub>1</sub></u>	<u>R<sub>2</sub></u>	
(3)			$\lambda_{\text{max}}(\text{EtOH}) = 366 \text{ nm}; \epsilon = 38\,894,$ $E(1\%, 1 \text{ cm}) = 837$
(7)			$\lambda_{\text{max}}(\text{EtOH}) = 366 \text{ nm}; \epsilon = 44\,209,$ $E(1\%, 1 \text{ cm}) = 1082$
(9)			$\lambda_{\text{max}}(\text{EtOH}) = 365 \text{ nm}; \epsilon = 38\,053,$ $E(1\%, 1 \text{ cm}) = 1079$

	General formula		
			
Comp. of formula	R <sub>1</sub>	R <sub>2</sub>	
(11)			$\lambda_{\max}(\text{EtOH}) = 366 \text{ nm}; \epsilon = 38\,273,$ $E (1\%, 1 \text{ cm}) = 823$
(13)			$\lambda_{\max}(\text{EtOH}) = 366 \text{ nm}; \epsilon = 36\,567,$ $E (1\%, 1 \text{ cm}) = 634$
(15)			$\lambda_{\max}(\text{EtOH}) = 355 \text{ nm}; \epsilon = 41\,401,$ $E (1\%, 1 \text{ cm}) = 1174$
(17)			$\lambda_{\max}(\text{EtOH}) = 364 \text{ nm}; \epsilon = 42\,514,$ $E (1\%, 1 \text{ cm}) = 1117$

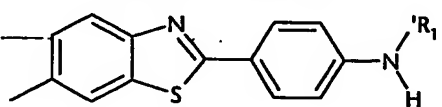
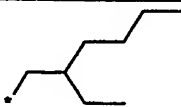


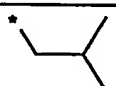
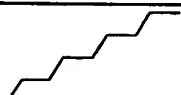

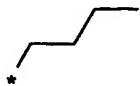

**Example 2: General work procedure for the synthesis of monoalkylated compounds of**

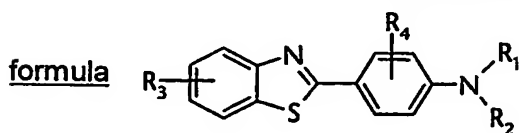
**formula**



0.12 mol of 2-(4-aminophenyl)-6-methylbenzothiazole is dissolved in 200 ml of absolute tetrahydrofuran and cooled to  $-10^{\circ}\text{C}$ . At from  $-5$  to  $-10^{\circ}\text{C}$ , 3.17 g (0.132 mol) of sodium hydride are added, in portions, to the solution. The reaction mixture is then stirred at  $10^{\circ}\text{C}$  for 30 minutes before 0.13 mol of the appropriate haloalkane dissolved in 200 ml of absolute tetrahydrofuran is added dropwise. After heating to boiling point, the reaction mixture is refluxed for about 20 hours until the reaction is complete. 10 ml of methanol are then added and the reaction mixture is concentrated to half its original volume using a rotary evaporator. After adding 200 ml of distilled water, the crude product is extracted with ethyl acetate. Subsequent column chromatography over silica gel using a mixture of cyclohexane and ethyl acetate yields the pure product, which is dried under a high vacuum at  $80^{\circ}\text{C}$  and 0.02 mbar.

The following compounds may be prepared by this method:

<p style="text-align: center;"><u>General formula</u></p> 		
Comp. of formula	$R_1$	
(4)		$\lambda_{\max}(\text{EtOH}) = 358 \text{ nm}; \epsilon = 39\,746, E(1\%, 1 \text{ cm}) = 1127$
(6)		$\lambda_{\max}(\text{EtOH}) = 356 \text{ nm}; \epsilon = 42\,328, E(1\%, 1 \text{ cm}) = 1397$
(8)		$\lambda_{\max}(\text{EtOH}) = 356 \text{ nm}; \epsilon = 38\,141, E(1\%, 1 \text{ cm}) = 1175$
(10)		$\lambda_{\max}(\text{EtOH}) = 357 \text{ nm}; \epsilon = 22\,669, E(1\%, 1 \text{ cm}) = 765$
(12)		$\lambda_{\max}(\text{EtOH}) = 356 \text{ nm}; \epsilon = 37\,927, E(1\%, 1 \text{ cm}) = 1076$
(14)		$\lambda_{\max}(\text{EtOH}) = 356 \text{ nm}; \epsilon = 38\,173, E(1\%, 1 \text{ cm}) = 934$
(16)		$\lambda_{\max}(\text{EtOH}) = 357 \text{ nm}; \epsilon = 37\,122, E(1\%, 1 \text{ cm}) = 1252$
(18)		$\lambda_{\max}(\text{EtOH}) = 355 \text{ nm}; \epsilon = 39\,164, E(1\%, 1 \text{ cm}) = 1459$

Example 3: General work procedure for the synthesis of compounds of

These compounds may be prepared by condensation of the appropriately  $R_3$ -substituted

o-aminothiophenols of formula with the appropriate  $R_1$ -,  $R_2$ - and  $R_4$ -

substituted p-aminobenzoic acid derivatives in a manner known *per se*, for example in accordance with DE 2 333 378 or E. Barni *et al.*, J. Heterocyclic Chem. 20, 1517-1521 (1983) or with the appropriate  $R_1$ -,  $R_2$ - and  $R_4$ -substituted p-aminobenzaldehyde derivatives, for example in accordance with DE 2 333 378 and the literature references cited herein.

The following compounds may be prepared by this method:

	<u>General formula</u>		
<u>Comp. of formula</u>	$R_1$	$R_2$	
(19)	H	H	$\lambda_{\max}(\text{EtOH}) = 358 \text{ nm}; \epsilon = 39\,095;$ $E(1\%, 1 \text{ cm}) = 1613$
(20)	$\text{C}_2\text{H}_5$	$\text{C}_2\text{H}_5$	$\lambda_{\max}(\text{EtOH}) = 381 \text{ nm}; \epsilon = 51\,869;$ $E(1\%, 1 \text{ cm}) = 1738$
(21)		H	$\lambda_{\max}(\text{EtOH}) = 3450 \text{ nm}; \epsilon = 35\,890$ $E(1\%, 1 \text{ cm}) = 1057$